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(54) Title: METHOD FOR THE ELECTROCHEMICAL DEPOSITION OF CARBON NANOTUBES

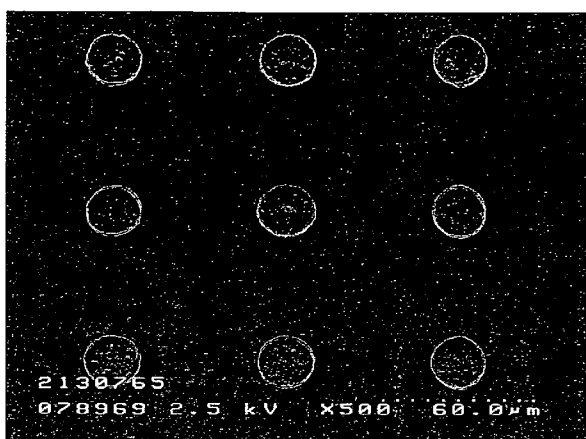


Figure 4. SEM image of CNT deposited on a PR patterned ITO substrate

(57) Abstract: This invention relates to the electrochemical deposition of carbon nanotubes (CNTs) on a substrate using an electrochemical cell. A dispersion of a complex of CNTs and an anionic polymer is neutralized and thereby caused to deposit on the anode plate of the cell.

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TITLEMETHOD FOR THE ELECTROCHEMICAL
DEPOSITION OF CARBON NANOTUBES

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This application claims the benefit of U.S. Provisional Application No. 60/903,260, filed 24 February 2007, which is by this reference incorporated
10 in its entirety as a part hereof for all purposes.

Technical Field

This invention relates to the electrochemical
15 deposition of carbon nanotubes ("CNTs") on a substrate.

Background

US 6,902,658 describes an electrophoretic
20 deposition method in which a separate step of depositing a binder material onto a substrate is performed prior to deposition thereon of CNTs. A need thus remains for a method in which CNTs and one or more accompanying materials may be deposited onto a
25 substrate simultaneously.

Summary

In one embodiment, this invention provides a
30 method for the deposition of carbon nanotubes by:

(a) providing an electrochemical cell that comprises a cathode, an anode plate, a first electrically conducting pathway connecting the cathode

to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate;

(b) providing as an aqueous electrolyte disposed between the cathode and the anode a dispersion of a complex formed from carbon nanotubes and a first anionic polymer; and

(c) applying a voltage to the electrochemical cell to deposit the complex on the anode.

In another embodiment, this invention provides a film that includes a substrate and, disposed on the substrate, (a) coagulant residue, and (b) a complex formed from carbon nanotubes and a first anionic polymer.

In a further embodiment, this invention provides a cathode assembly for a field emission device comprising a film as described above.

In yet another embodiment, this invention provides a field emission device comprising a cathode assembly as described above.

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Brief Description of the Drawings

Figure 1 shows a schematic representation of the mechanism of deposit in one embodiment of the methods of this invention.

Figure 2 shows deposited material on a film as prepared in Example 1.

Figure 3 shows the configuration of an

electrochemical cell as used in the examples.

Figure 4 shows deposited material on a film as prepared in Example 2.

Figure 5 shows an image of phosphor illumination from a film as tested in Example 3.

Figure 6 shows a plot of recorded anode current and anode voltage values as obtained in Example 4.

Figure 7 shows an image of phosphor illumination from a film as tested in Example 4.

Figure 8 shows an image of phosphor illumination from a film as tested in Example 5.

15 Detailed Description

CNTs are well known to have unique and useful electrical properties, and are frequently used in the fabrication of the cathode of a field emission device. However, adoption of these materials is constrained by their high cost. Therefore, an objective of the invention is to provide a process for making a uniform CNT film on a substrate such as a conducting substrate with good uniformity and low material consumption. A further objective is to pattern the CNT film thus prepared to be useful in electronic applications. The CNT film so made may be used in a cathode assembly that is installed in a field emission device.

A CNT film is made by the method of this invention by the deposition of CNTs on a substrate by electrochemical means, and for such purpose the method hereof involves the use of an electrochemical cell. The cell contains a cathode, an anode plate, a first

electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate. An aqueous electrolyte is provided to the cell and is disposed between the cathode and the anode. Contained in the electrolyte is a dispersion of a complex formed from CNTs and a first anionic polymer, and optionally a coagulant.

10

CNTs as used herein are generally about 0.5-2 nm in diameter where the ratio of the length dimension to the narrow dimension, *i.e.* the aspect ratio, is at least 5. In general, the aspect ratio is between 10 and 2000. CNTs are comprised primarily of carbon atoms, however may be doped with other elements, *e.g.* metals. The carbon-based nanotubes of the invention can be either multi-walled nanotubes (MWNTs) or single-walled nanotubes (SWNTs). A MWNT, for example, includes several concentric nanotubes each having a different diameter. Thus, the smallest diameter tube is encapsulated by a larger diameter tube, which in turn, is encapsulated by another larger diameter nanotube. A SWNT, on the other hand, includes only one nanotube.

CNTs may be produced by a variety of methods, and are additionally commercially available. Methods of CNT synthesis include laser vaporization of graphite [A. Thess *et al*, *Science* 273, 483 (1996)], arc discharge [C. Journet *et al*, *Nature* 388, 756 (1997)] and HiPCo (high pressure carbon monoxide) process [P. Nikolaev *et al*, *Chem. Phys. Lett.* 313, 91-97 (1999)].

Chemical vapor deposition (CVD) can also be used in producing carbon nanotubes [J. Kong et al, Chem. Phys. Lett. 292, 567-574 (1998); J. Kong et al, Nature 395, 878-879 (1998); A. Cassell et al, J. Phys. Chem. 103, 6484-6492 (1999); H. Dai et al, J. Phys. Chem. 103, 11246-11255 (1999)]. Additionally CNTs may be grown via catalytic processes both in solution and on solid substrates [Yan Li et al, Chem. Mater.; 2001; 13(3); 1008-1014); (N. Franklin and H. Dai, Adv. Mater. 12, 890 (2000); A. Cassell et al, J. Am. Chem. Soc. 121, 7975-7976 (1999)].

A major obstacle to the use of CNTs has been the diversity of tube diameters, chiral angles, and aggregation states in nanotube samples obtained from the various preparation methods. Aggregation is particularly problematic because the highly polarizable, smooth-sided fullerene tubes readily form parallel bundles or ropes with a large van der Waals binding energy. This bundling perturbs the electronic structure of the tubes, and it confounds almost all attempts to separate the tubes by size or type or to use them as individual macromolecular species.

There is provided by this invention a method for dispersing a population of bundled carbon nanotubes by contacting the bundled nanotubes with an aqueous solution of an anionic polymer. A complex containing the anionic polymer and the CNTs is thereby formed, but the association between the anionic polymer and the CNTs in the complex is a loose association, is formed essentially by van der Waals bonds or some other non-covalent means, and is not formed through the

interaction of specific functionalized groups. The structural integrity of the CNTs is therefore retained, but the complexes they form with the anionic polymers become suspended in a dispersion in the electrolyte.

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A variety of anionic polymers may thus be used as dispersants for the purpose of dispersing CNTs in an aqueous solution by facilitating the formation of the polymer/CNT complex, but a preferred polymer for use for such purpose is a nucleic acid, particularly a stabilized solution of nucleic acid molecules. Nucleic acids are very effective in dispersing CNTs by the formation of nanotube-nucleic acid complexes based on non-covalent interactions between the nanotube and the nucleic acid molecule. The method of this invention therefore includes a method for the dispersion of bundled CNTs by contacting the nanotubes with a solution of anionic polymers such as nucleic acid molecules.

20

In the following discussion of the use of nucleic acid molecules to form complexes with and thereby disperse CNTs, the following terms and abbreviations are used:

25

"cDNA" means complementary DNA

"PNA" means peptide nucleic acid

"SEM" means scanning electron microscopy

"ssDNA" means single stranded DNA

"tRNA" means transfer RNA

30

"CNT" means carbon nanotube

"MWNT" means multi-walled nanotube

"SWNT" means single walled nanotube

"TEM" means transmission electron microscopy

A "nucleic acid molecule" is defined as a polymer of RNA, DNA, or peptide nucleic acid (PNA) that is single- or double-stranded, optionally containing
5 synthetic, non-natural or altered nucleotide bases. A nucleic acid molecule in the form of a polymer of DNA may be comprised of one or more segments of cDNA, genomic DNA or synthetic DNA.

10 The letters "A", "G", "T", "C" when referred to in the context of nucleic acids will mean the purine bases adenine ($C_5H_5N_5$) and guanine ($C_5H_5N_5O$) and the pyrimidine bases thymine ($C_5H_6N_2O_2$) and cytosine ($C_4H_5N_3O$), respectively.

15

The term "peptide nucleic acids" refers to a material having stretches of nucleic acid polymers linked together by peptide linkers.

20

A "stabilized solution of nucleic acid molecules" refers to a solution of nucleic acid molecules that are solubilized and in a relaxed secondary conformation.

25

A "nanotube-nucleic acid complex" means a composition comprising a carbon nanotube loosely associated with at least one nucleic acid molecule. Typically the association between the nucleic acid and the nanotube is by van der Waals bonds or some other
30 non-covalent means.

The term "agitation means" refers to a devices that facilitate the dispersion of nanotubes and

nucleic acids. A typical agitation means is sonication.

The term "denaturant" refers to substances effective in the denaturation of DNA and other nucleic acid molecules.

Standard recombinant DNA and molecular biology techniques used here are well known in the art and are described by Sambrook, J., Fritsch, E. F. and Maniatis, T., Molecular Cloning: A Laboratory Manual, Second Edition, Cold Spring Harbor Laboratory Press, Cold Spring Harbor, NY (1989) (hereinafter "Maniatis"); by Silhavy, T. J., Bannan, M. L. and Enquist, L. W., Experiments with Gene Fusions, Cold Spring Harbor Laboratory Cold Press Spring Harbor, NY (1984); and by Ausubel, F. M. et al., Current Protocols in Molecular Biology, published by Greene Publishing Assoc. and Wiley-Interscience (1987).

20

Nucleic acid molecules as used in a method of this invention may be of any type and from any suitable source and include but are not limited to DNA, RNA and peptide nucleic acids. The nucleic acid molecules used herein may be generated by synthetic means or may be isolated from nature by protocols well known in the art (*Sambrook supra*). The nucleic acid molecules may be either single stranded or double stranded and may optionally be functionalized at any point with a variety of reactive groups, ligands or agents. Functionalization of nucleic acids is not, however, required for their association with CNTs for the purpose of dispersion, and most of the nucleic acids

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used herein for dispersion do lack functional groups and are therefore referred to herein as "unfunctionalized".

5 Peptide nucleic acids (PNA) are particularly useful herein for dispersion as they possess the double functionality of both nucleic acids and peptides. Methods for the synthesis and use of PNA's are well known in the art, see for example Antsyrovitch, S. I.,
10 Peptide nucleic acids: Structure, Russian Chemical Reviews (2002), 71(1), 71-83.

 The nucleic acid molecules used herein may have any composition of bases and may even consist of
15 stretches of the same base (poly A or polyT for example) without impairing the ability of the nucleic acid molecule to disperse the bundled CNTs. Preferably the nucleic acid molecules will be less than about 2000 bases where less than 1000 bases is
20 preferred and where from about 5 bases to about 1000 bases is most preferred. Generally the ability of nucleic acids to disperse CNTs appears to be independent of sequence or base composition, however there is some evidence to suggest that the less G-C and
25 T-A base-pairing interactions in a sequence, the higher the dispersion efficiency, and that RNA and varieties thereof is particularly effective in dispersion and is thus preferred herein. Nucleic acid molecules suitable for use herein include without limitation
30 those having the general formula:

1. An wherein n = 1 - 2000;
2. Tn wherein n = 1 - 2000;
3. Cn wherein n = 1 - 2000;
4. Gn wherein n = 1 - 2000;
5. Rn wherein n = 1-2000, and wherein R may be either A or G;
6. Yn wherein n = 1 - 2000, and wherein Y may be either C or T;
7. Mn wherein n = 1 - 2000, and wherein M may be either A or C;
8. Kn wherein n = 1 - 2000, and wherein K may be either G or T;
9. Sn wherein n = 1 - 2000, and wherein S may be either C or G;
10. Wn wherein n = 1 - 2000, and wherein W may be either A or T;
11. Hn wherein n = 1 - 2000, and wherein H may be either A or C or T;
12. Bn wherein n = 1 -2000, and wherein B may be either C or G or T;
13. Vn wherein n = 1 - 2000, and wherein V may be either A or C or G;
14. Dn wherein n = 1 - 2000, and wherein D may be either A or G or T; and
15. Nn wherein n = 1 - 2000, and wherein N may be either A or C or T or G.

In addition to the combinations listed above, any of these sequences may have one or more deoxyribonucleotides replaced by ribonucleotides (i.e. RNA or RNA/DNA hybrid) or one or more sugar-phosphate linkages replaced by peptide bonds (i.e. PNA or PNA/RNA/DNA hybrid).

Nucleic acid molecules as used herein may be stabilized in a suitable solution. It is preferred that the nucleic acid molecules be in a relaxed secondary conformation and only loosely associated with each other to allow for the greatest contact by individual strands with the CNTs. Stabilized solutions of nucleic acids are common and well known in the art (see *Sambrook, supra*) and typically include salts and buffers such as sodium and potassium salts, and TRIS (Tris(2-aminoethyl)amine), HEPES (N-(2-hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid), and MES(2-(N-Morpholino)ethanesulfonic acid). Preferred solvents for stabilized nucleic acid solutions are those that are water miscible where water is most preferred. The process of dispersion may be improved with the optional addition of nucleic acid denaturing substances to the solution. Common denaturants include but are not limited to formamide, urea and guanidine. A non-limiting list of suitable denaturants may be found in *Sambrook, supra*.

To prepare a dispersion according to a method hereof, one or more nucleic acid molecules may be contacted with a population of bundled carbon nanotubes. It is preferred, although not required, contact be made in the presence of an agitation means of some sort. Typically the agitation means employs sonication, but may also include devices that produce high shear mixing of the nucleic acids and CNTs (*i.e.* homogenization), or any combination thereof. Upon agitation, the CNTs will become dispersed and will form nanotube-nucleic acid complexes comprising at least one

nucleic acid molecule loosely associated with the CNT by hydrogen bonding or some other non-covalent means.

Temperature during the process of contacting
5 CNTs with a nucleic acid may have an effect on the efficacy of the dispersion. Mixing at room temperature or higher has been seen to give longer dispersion times whereas mixing at temperatures below room temperature (23°C) has been seen to give more
10 rapid dispersion times, and temperatures of about 4°C are preferred. The dispersion of CNTs by contact with nucleic acid molecules is also described in US 2004/0132072 and US 2004/0146904, each of which is by this reference incorporated in its entirety as a part
15 hereof for all purposes.

In addition to the nucleic acid molecules described above, one or more other anionic polymers may be used for the purpose of preparing an aqueous
20 dispersion of CNTs. Examples of other anionic polymers that have been found useful in the preparation of a dispersion of CNTs include without limitation ionized poly(acrylic acid) ("PAA") or ionized ethylene/(meth)acrylic acid copolymer ("EAA" or
25 "EMAA"), either of which may be neutralized with cations such as Na⁺, K⁺, NH₄⁺ or Cr⁺; styrenic ionomers such as styrene/sodium styrene sulfonate copolymer (PSS) or styrene/sodium styrene methacrylate copolymer; and ionized tetrafluoroethylene/sulfonic acid
30 copolymers such as Nafion™ copolymer (from DuPont) in which the sulfonic acid group in a tetrafluoroethylene/perfluorovinyl ether copolymer may be sodium neutralized. As indicated above with

respect to nucleic acid molecules, ultrasonication or other mixing means may be applied to facilitate the dispersion of CNTs in an aqueous solution of one or more of the anionic polymers discussed in this
5 paragraph.

In one embodiment, deposition on the anode plate of the cell of the complexes formed from CNTs and molecules of an anionic polymer, as dispersed in the
10 electrolyte solution contained in the cell, will be facilitated by the presence therein of the optional coagulant. The coagulant will neutralize the negative charge on the anionic polymer in the complex. As the population of anionic polymer/CNT complexes has been
15 maintained in dispersion primarily by the repulsion of one negatively charged complex from another (or by the repulsion of positively charged double layers surrounding the complexes), neutralization of those negative charges (or compression of the double layer)
20 by the coagulant will remove the force enabling the population of complexes to remain in dispersion in the electrolyte solution. As the action of the coagulant to neutralize the complexes occurs in close proximity to the anode plate, the complexes (as no longer
25 dispersed) will in varying degrees undergo a transition from solution phase to solid phase, become progressively aggregated and agglomerated (similar to the formation of floccules and flocs), and then be collected and deposited on the surface of the anode
30 plate. In addition to the CNT complexes, the material as deposited on the plate may include coagulant residue.

If first and second anionic polymers are present in the electrolyte solution, such as a first polymer that forms a complex with CNTs and a second polymer that does not or is more loosely associated with CNTs than the first polymer, they may become deposited on the surface of the anode at the same time. The first polymer may, for example, be deposited in a matrix of the second polymer. If additional materials needed to enhance the usefulness and performance of the anode plate in a field emission device, such as conductive or functionalized particles, are present in the electrolyte solution, they may be deposited on the anode plate at the same time as the anionic polymer/CNT complexes. Figure 2 shows a typical example of the type of film formed by such deposition on the anode plate, which film has good uniformity of evenly deposited, well-adhered material all across its surface.

Coagulants suitable for use herein for the purpose of neutralizing an anionic polymer/CNT complex include inorganic coagulants such as trivalent cations formed from metals including Group VIII/VIIIA metals such as iron, cobalt, ruthenium or osmium. As a trivalent cation can be up to as much as ten times more effective in neutralizing the complex than a divalent cation, a convenient way to provide the coagulant is to supply a divalent cation such as tris(2,2'-bipyridyl)dichloro-ruthenium (II) to the electrolyte solution wherein the 2⁺ cation is oxidized to a 3⁺ valence by the loss of electrons to the anode plate. A schematic representative of this mechanism is shown in Figure 1.

In an alternative embodiment, however, a coagulant is not used where the anode plate is formed from a metal such as silver or nickel. In such case, the metal on the plate dissolves in the electrolyte solution, and the charge on an anionic polymer/CNT complex is neutralized by cations formed from metal atoms that have gone into solution from the solid metal from which the plate is formed.

10

The method hereof is generally performed by operation of the cell at lower potential such as less than about 5 volts, or from about 2 to less than about 5 volts, or from about 2 volts to about 3 volts. Thickness of the deposited film is to a large extent directly related to length of deposition time. A deposition time in the range of about 1 to about 10 minutes, or in the range of about 1 to about 2 minutes, may be used. A positive potential is maintained at the anode plate relative to the cathode of the cell.

The method hereof may be used to produce a film in which the deposited material is deposited in a pre-determined pattern. This may be accomplished by patterning the surface of the plate used as the anode using conventional photoimaging techniques. Thus a photoresist may be activated through a mask and then developed to provide on the surface of the anode a pattern such as an array of circular wells. As the anionic polymer/CNT complexes are aggregated and settle out of solution, they are deposited only in the holes, and the photoresist may be removed. This provides a patterned CNT film, with the anode plate serving as a

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substrate for the film, for use by installation in a field emission device.

After completion of the deposition of CNT
5 complex material on the anode plate in the cell, the plate may be removed from the cell, rinsed, dried and installed in such condition in a field emission device for use as part of the cathode assembly therein to provide electron emission. Alternatively, however,
10 the plate may be baked and/or fired before installation in a field emission device to melt the deposited polymer(s) and utilize them in that form as an adhesive to more securely anchor the CNTs to the surface of the plate, resulting in a CNT-containing film with
15 excellent abrasion resistance.

In the field emission device into which the above described plate coated with deposited material may be installed, an electron emitting material is
20 disposed on a cathode and, when energized, bombards an anode with electrons. The electron emitting material may be an acicular substance such as carbon, a semiconductor, a metal or mixtures thereof. As used herein, "acicular" means particles with aspect ratios
25 of 10 or more. Typically, glass frit, metallic powder or metallic paint or a mixture thereof is used to attach the electron emitting material to a substrate in the cathode assembly.

30 Acicular carbon as used as the electron emitting material may be of various types, but carbon nanotubes are the preferred acicular carbon and single wall CNTs are especially preferred. Carbon fibers

grown from the catalytic decomposition of carbon-containing gases over small metal particles are also useful as acicular carbon, and other examples of acicular carbon are polyacrylonitrile-based (PAN-based) carbon fibers and pitch-based carbon fibers.

Various processes can be used to attach an electron emitting material to a substrate. The means of attachment must withstand and maintain its integrity under the conditions of manufacturing the apparatus into which the field emitting cathode is placed and under the conditions surrounding its use, e.g. typically vacuum conditions and temperatures up to about 450°C. A preferred method is to screen print a paste comprised of the electron emitting material and glass frit, metallic powder or metallic paint or a mixture thereof onto a substrate in the desired pattern and to then fire the dried patterned paste. For a wider variety of applications, e.g. those requiring finer resolution, the preferred process comprises screen printing a paste which further comprises a photoinitiator and a photohardenable monomer, photopatterning the dried paste and firing the patterned paste.

The substrate can be any material to which the paste composition will adhere. If the paste is non-conducting and a non-conducting substrate is used, a film of an electrical conductor to serve as the cathode electrode and provide means to apply a voltage to the electron emitting material will be needed. Silicon, a glass, a metal or a refractory material such as alumina can serve as the substrate. For display

applications, the preferable substrate is glass and soda lime glass is especially preferred. For optimum conductivity on glass, silver paste can be pre-fired onto the glass at 500-550°C in air or nitrogen, but preferably in air. The conducting layer so-formed can then be over-printed with the emitter paste.

The paste used for screen printing typically contains the electron emitting material, an organic medium, solvent, surfactant and either low softening point glass frit, metallic powder or metallic paint or a mixture thereof. The role of the medium and solvent is to suspend and disperse the particulate constituents, *i.e.* the solids, in the paste with a proper rheology for typical patterning processes such as screen printing. There are many organic media known for use for such purpose including cellulosic resins such as ethyl cellulose and alkyd resins of various molecular weights. Butyl carbitol, butyl carbitol acetate, dibutyl carbitol, dibutyl phthalate and terpineol are examples of useful solvents. These and other solvents are formulated to obtain the desired viscosity and volatility requirements.

A glass frit that softens sufficiently at the firing temperature to adhere to the substrate and to the electron emitting material is also used. A lead or bismuth glass frit can be used as well as other glasses with low softening points such as calcium or zinc borosilicates. If a screen printable composition with higher electrical conductivity is desired, the paste may also contain a metal, for example, silver or gold. The paste typically contains about 40 wt % to

about 80 wt % solids based on the total weight of the paste. These solids include the electron emitting material and glass frit and/or metallic components. Variations in the composition can be used to adjust the
5 viscosity and the final thickness of the printed material.

The emitter paste is typically prepared by three-roll milling a mixture of the electron emitting
10 material, organic medium, surfactant, solvent and either low softening point glass frit, metallic powder or metallic paint or a mixture thereof. The paste mixture can be screen printed using, for example, a 165-400-mesh stainless steel screen. The paste can be
15 deposited as a continuous film or in the form of a desired pattern. When the substrate is glass, the paste is then fired at a temperature of about 350°C to about 550°C, preferably at about 450°C to about 525°C, for about 10 minutes in nitrogen. Higher firing
20 temperatures can be used with substrates which can endure them provided the atmosphere is free of oxygen. However, the organic constituents in the paste are effectively volatilized at 350-450°C, leaving a layer of the composite of the electron emitting material and
25 glass and/or metallic conductor. The electron emitting material appears to undergo no appreciable oxidation or other chemical or physical change during the firing in nitrogen.

30 If the screen-printed paste is to be photopatterned, the paste may also contain a photoinitiator, a developable binder and a photohardenable monomer comprised, for example, of at

least one addition polymerizable ethylenically unsaturated compound having at least one polymerizable ethylenic group. Typically, a paste prepared from an electron emitting material such as CNTs, silver and glass frit will contain about 0.01-6.0 wt % nanotubes, about 40-75 wt % silver in the form of fine silver particles and about 3-15 wt % glass frit based on the total weight of the paste.

The anode of the field emission device is an electrode coated with an electrically conductive layer. When the field emission device is used in a display device where the cathode contains an array of pixels of the thick film paste deposits described above, the anode in the display device may comprise phosphors to convert incident electrons into light. The substrate of the anode would also be selected to be transparent so that the resulting light could be transmitted. From the cathode assembly and anode, a sealed unit is constructed in which the cathode assembly and anode are separated by spacers, and there is an evacuated space between the anode and the cathode. This evacuated space needs to be under partial vacuum so that the electrons emitted from the cathode may transit to the anode with only a small number of collisions with gas molecules. Frequently the evacuated space is evacuated to a pressure of less than 10^{-5} Torr.

Such a field emission device is useful in a variety of electronic applications, e.g. vacuum electronic devices, flat panel computer and television displays, back-light source for LCD displays, emission gate amplifiers, and klystrons and in lighting devices.

For example, flat panel displays having a cathode using a field emission electron source, i.e. a field emission material or field emitter, and a phosphor capable of emitting light upon bombardment by electrons emitted by the field emitter have been proposed. Such displays have the potential for providing the visual display advantages of the conventional cathode ray tube and the depth, weight and power consumption advantages of the other flat panel displays. The flat panel displays can be planar or curved. U.S. Patents 4,857,799 and 5,015,912 disclose matrix-addressed flat panel displays using micro-tip cathodes constructed of tungsten, molybdenum or silicon. WO 94-15352, WO 94-15350 and WO 94-28571 disclose flat panel displays wherein the cathodes have relatively flat emission surfaces.

These devices are also described in US 2002/0074932, which is by this reference incorporated in its entirety as a part hereof for all purposes.

Materials as used in the process hereof may be made by processes known in the art, or are available commercially from suppliers such as Alfa Aesar (Ward Hill, Massachusetts), City Chemical (West Haven, Connecticut), Fisher Scientific (Fairlawn, New Jersey), Sigma-Aldrich (St. Louis, Missouri) or Stanford Materials (Aliso Viejo, California).

The advantageous attributes and effects of this invention may be seen in a series of examples (Examples 1 ~ 5), as described below. The embodiments on which the examples are based are representative only, and the selection of those embodiments to illustrate the invention does not indicate that

materials, conditions, specifications, components, reactants, techniques and protocols not described in these examples are not suitable for practicing this invention, or that subject matter not described in
5 these examples is excluded from the scope of the appended claims and equivalents thereof.

Examples

10

150 mg of laser-ablated CNTs (from CNI, Houston, Texas) was mixed with 30 mg yeast RNA (from Sigma Aldrich) in 15 mL of 1X TBE [tris borate (ethylenediaminetetraacetic acid)] buffer (from Sigma
15 Aldrich). The mixture was sonicated with a probe sonicator at a power level of 20W for 30 min. The resulting dispersion was mixed with two other components according to the following table (Table 1) to make up 100 mL of deposition solution. $\text{Ru}^{2+}(\text{bipy})_3$
20 as used in the deposition solution is tris(2,2'-bipyridyl)dichloro-ruthenium (II) and is obtained from Sigma Aldrich. EMMA is ethylene/methacrylic acid ionomer obtained from DuPont as Surlyn™ ionomer.

Table 1.
Composition of deposition solution

Component	Stock conc.	Volume added	Final conc.
CNT dispersion	10mg/mL	4 mL	0.04 %
EMMA	10 mg /mL	2 mL	0.02%
Ru ²⁺ (bipy) ₃	10 mM	2 mL	0.2 mM
water		92 mL	

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Example 1

A 2' x 2' stainless steel plate (used as the cathode) and a 2' x 2' indium tin oxide ("ITO") plate (used as the anode) were inserted in a parallel fashion into a rectangular electrochemical cell (the configuration for which is shown in Fig. 3). The cell was charged with 15 mL of the deposition solution as the electrolyte. A potential difference of 3.2 V was applied between the two electrodes. After 1 minute, the deposition was stopped, and the ITO plate was taken out of the cell, rinsed with deionized water and dried in air. Uniform deposition of material on the plate was obtained as shown in Fig. 2.

Example 2

A photoresist (PR) patterned indium tin oxide (ITO) substrate (2' x 2') was used as the anode. The PR layer defines an array of circular wells with 20 um

diameter. The wells expose the surface of the ITO plate for CNT deposition. Before electrodeposition, the PR coated ITO plate was dipped into a solution of 0.01% Triton X-100, taken out and dried by blowing N₂ gas. This assists with coating the hydrophobic PR layer with a thin hydrophilic layer for better wetting. After this treatment, a 2' x 2' stainless steel plate (used as the cathode) and the PR-coated ITO plate (used as the anode) were inserted in a parallel fashion into the same type of electrochemical cell as used in Example 1. The cell was charged with 15 mL of the deposition solution. An AC potential (100 Hz square wave with 0 to 3.5 V peak-to-peak voltage and 50% duty cycle) was applied between the two electrodes. After 1 minute, the deposition was stopped, and the ITO plate was taken out of the cell, rinsed with deionized water and dried in air. The PR layer was removed by treatment with an acetone solvent. Good uniformity of deposition of CNT material in the exposed wells was obtained as shown in Fig. 4.

Example 3

The dried plate obtained from Example 1 and depicted in Figure 2 was then fired in nitrogen for 10 minutes at 420°C. A piece of adhesive tape was then laminated over the CNT film and subsequently removed. This process, commonly referred to as "activation", is known to fracture the film surface exposing and lifting the CNT filaments off the substrate surface to dramatically enhance electron field emission. A diode field emission device was then assembled by using the CNT film coated ITO

substrate as a cathode. Opposite to this "activated" cathode, an anode plate consisting of an ITO coated glass substrate with a phosphor coating was mounted. Electrically insulating spacers 1 mm thick were used to
5 maintain a distance between the cathode and anode substrates. Electrical contact was made to the cathode and anode electrodes using silver paint and copper tape to complete the diode device. The device was mounted in a vacuum chamber which was evacuated to
10 a pressure of $<1 \times 10^{-5}$ Torr. A pulsed square wave with a repetition rate of 60 Hz and a pulse width of 60 μ s was applied to the anode electrode. The cathode electrode was maintained at ground potential. At an anode voltage of 2 kV, an anode current of 200 μ A was
15 obtained. An image of phosphor illumination by electrons emitted by this device is shown in Figure 5.

Example 4

20 The dried plate obtained from Example 2 and depicted in Figure 4 was fired in nitrogen for 10 minutes at 420°C as described in Example 3. The CNT dot surfaces were activated with a piece of adhesive tape as described in Example 3. A diode
25 field emission device was then assembled by using the CNT dot covered ITO substrate as a cathode and an ITO coated glass substrate with a phosphor coating as anode. Glass spacers 0.22 mm thick were used in this example to maintain a distance between the cathode and
30 anode substrates. The device was mounted in a vacuum chamber which was evacuated to a pressure of $<1 \times 10^{-5}$ Torr. A pulsed square wave with a repetition rate of 60 Hz and a pulse width of 60 μ s was applied to the

anode electrode. The cathode electrode was maintained at ground potential. When the pulsed anode voltage reached 800 V, an average anode current of 5 μ A was measured. As the pulse anode voltage was increased, increasing anode current was measured. At an anode voltage of 925 V, an anode current of 40 μ A was obtained. Figure 6 shows a plot of the recorded anode current and anode voltage values from this field emission device. An image of phosphor illumination by electrons emitted by this device, operating at 975 V anode voltage and 80 μ A anode current, is shown in Figure 7. Each rectangular illuminated pixel on the anode was produced by an array of multiple CNT dots on the cathode.

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Example 5

Instead of a plain ITO coated glass substrate as was made in Example 2 and used in Example 4, the method hereof was used to deposit CNT dots on a top-gate triode substrate. A top-gate triode substrate typically consists of two conductive layers between which is disposed an insulating layer. In this example, an ITO coated glass substrate was used as the substrate for the top-gate triode, using the ITO layer as the cathode. An insulating dielectric layer was deposited on top of the ITO layer. A metallic gate electrode layer was deposited on the dielectric layer. In addition, an array of circular wells was etched through the metal and dielectric layers, using a photoresist ("PR") and mask, exposing the ITO surface. As in Example 2, the array of circular wells defined a pattern on the PR layer that covered the triode

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assembly. The openings of the wells in the PR had a smaller diameter than the diameter of the wells that extended through the metal and dielectric layer, but the circumference of the smaller well was concentric
5 with that of the larger. Using procedures similar to those described in Examples 2 and 4, CNT dots were deposited on the ITO surface, fired and activated.

Opposite the activated triode cathode, an
10 anode plate consisting of an ITO coated glass substrate with a phosphor coating was mounted. Spacers 3 mm thick were used to maintain the distance between the cathode and anode substrates. Electrical contact was made to the ITO cathode electrode, metal gate
15 electrode, and ITO anode electrode using silver paint and copper tape to complete a top-gate triode device. The device was mounted in a vacuum chamber which was evacuated to a pressure of $<1 \times 10^{-5}$ Torr. A DC voltage of 3 kV was applied to the anode electrode. A pulsed
20 square wave with a repetition rate of 120 Hz and a pulse width of 30 μ s was applied to the gate electrode. The cathode electrode was maintained at ground potential. When the pulsed gate voltage reached 70 V, an average anode current density of 5.0 μ A/cm² was
25 measured. An image of phosphor illumination by electrons emitted by this triode device is shown in Figure 8.

30 Features of certain of the devices of this invention are described herein in the context of one or more specific embodiments that combine various such features together. The scope of the invention is not,

however, limited by the description of only certain features within any specific embodiment, and the invention also includes (1) a subcombination of fewer than all of the features of any described embodiment, 5 which subcombination may be characterized by the absence of the features omitted to form the subcombination; (2) each of the features, individually, included within the combination of any described embodiment; and (3) other combinations of 10 features formed by grouping only selected features of two or more described embodiments, optionally together with other features as disclosed elsewhere herein.

In this specification, unless explicitly 15 stated otherwise or indicated to the contrary by the context of usage, where an embodiment of the subject matter hereof is stated or described as comprising, including, containing, having, being composed of or being constituted by or of certain features or 20 elements, one or more features or elements in addition to those explicitly stated or described may be present in the embodiment. An alternative embodiment of the subject matter hereof, however, may be stated or described as consisting essentially of certain features 25 or elements, in which embodiment features or elements that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of the subject matter hereof may be stated 30 or described as consisting of certain features or elements, in which embodiment, or in insubstantial variations thereof, only the features or elements specifically stated or described are present.

Claims

5 What is claimed is:

1. A method for the deposition of carbon nanotubes, comprising:

(a) providing an electrochemical cell that
10 comprises a cathode, an anode plate, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate;

15 (b) providing as an aqueous electrolyte disposed between the cathode and the anode a dispersion of a complex formed from carbon nanotubes and a first anionic polymer; and

(c) applying a voltage to the
20 electrochemical cell to deposit the complex on the anode.

2. A method according to Claim 1 wherein the aqueous electrolyte further comprises a coagulant.

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3. A method according to Claim 2 wherein coagulant residue is deposited on the anode together with the complex.

30 4. A method according to Claim 1 wherein the first polymer comprises a nucleic acid molecule.

5. A method according to Claim 1 wherein the

first polymer comprises RNA.

6. A method according to Claim 1 wherein the electrolyte further comprises a second anionic polymer.

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7. A method according to Claim 6 wherein the second ionic polymer comprises a styrenic ionomer or an ionized ethylene/(meth)acrylic acid copolymer.

10 8. A method according to Claim 6 wherein the complex, as deposited on the anode, is deposited in a matrix of the second anionic polymer.

15 9. A method according to Claim 7 wherein the first polymer comprises a nucleic acid molecule.

10. A method according to Claim 7 wherein the first polymer comprises RNA.

20 11. A method according to Claim 1 further comprising a step of removing the anode plate from the cell, and installing it in a field emission device.

25 12. A film comprising a substrate and, disposed on the substrate, (a) coagulant residue, and (b) a complex formed from carbon nanotubes and a first anionic polymer.

30 13. A method according to Claim 12 wherein the first polymer comprises a nucleic acid molecule.

14. A method according to Claim 12 wherein the first polymer comprises RNA.

15. A film according to Claim 12 wherein there is further disposed on the substrate a second anionic polymer.

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16. A method according to Claim 15 wherein the second ionic polymer comprises a styrenic ionomer or an ionized ethylene/(meth)acrylic acid copolymer.

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17. A method according to Claim 15 wherein the first polymer comprises a nucleic acid molecule.

18. A method according to Claim 15 wherein the first polymer comprises RNA.

15

19. A cathode assembly for a field emission device comprising a film according to Claim 1.

20. A field emission device comprising a cathode assembly according to Claim 19.

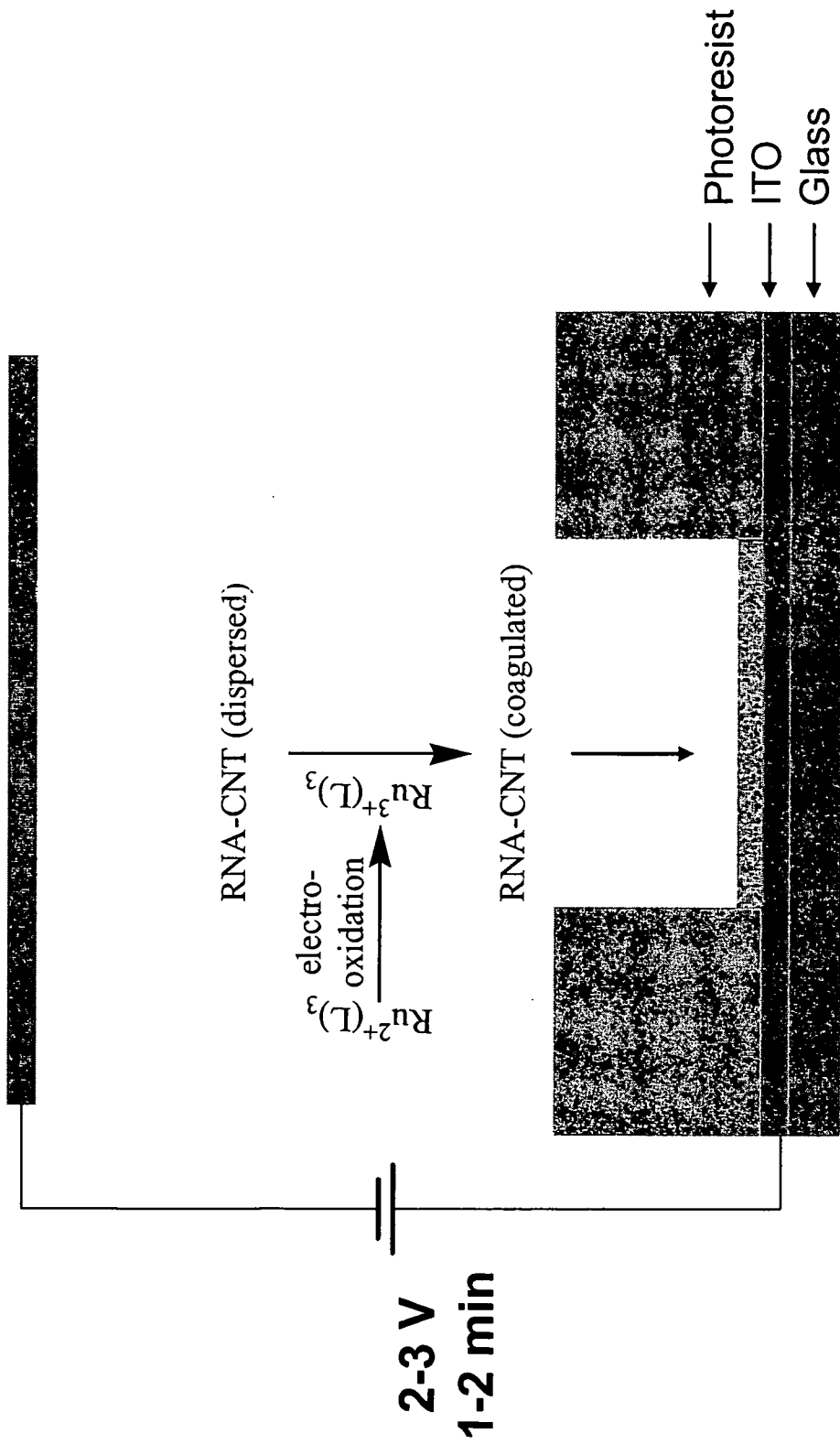
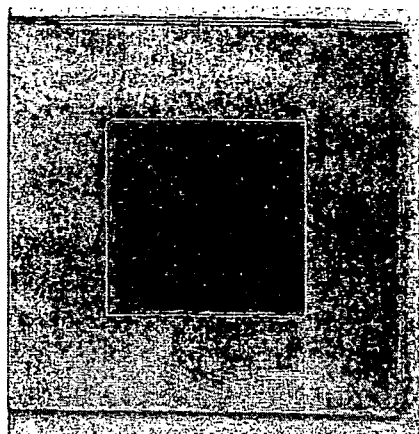


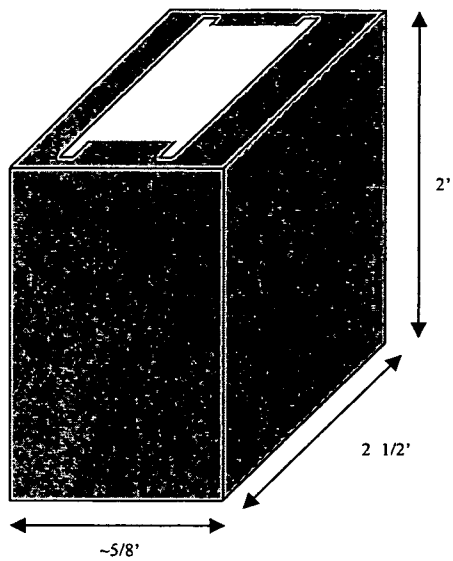
Figure 1



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Figure 2. Image of a continuous CNT film deposited on a bare ITO substrate

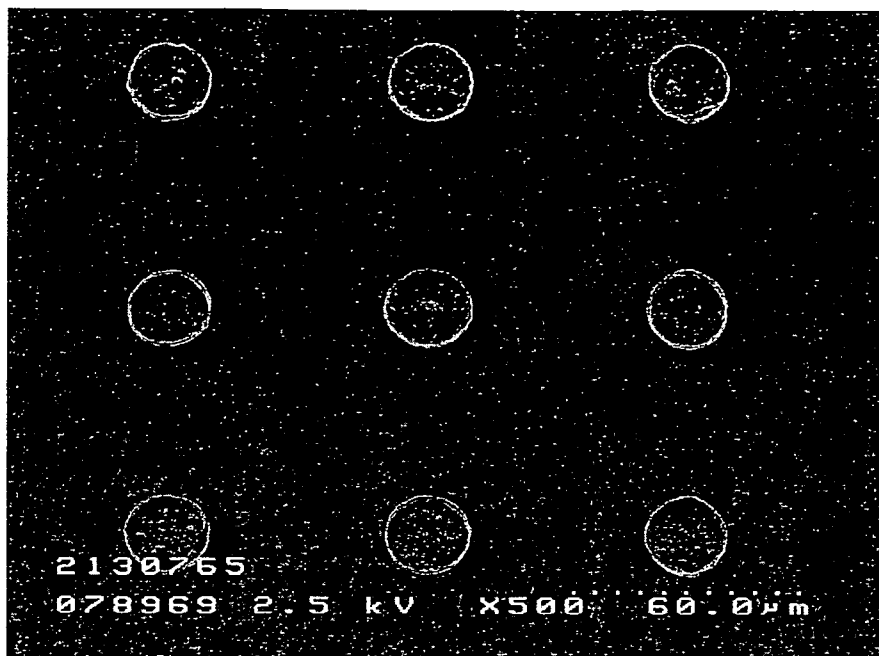
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Figure 3. Geometry of the electrochemical cell used in the Examples

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Figure 4. SEM image of CNT deposited on a PR patterned ITO substrate

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Figure 5: An image of the phosphor illumination by the field emission electrons from a continuous CNT film as disclosed in Example 3.

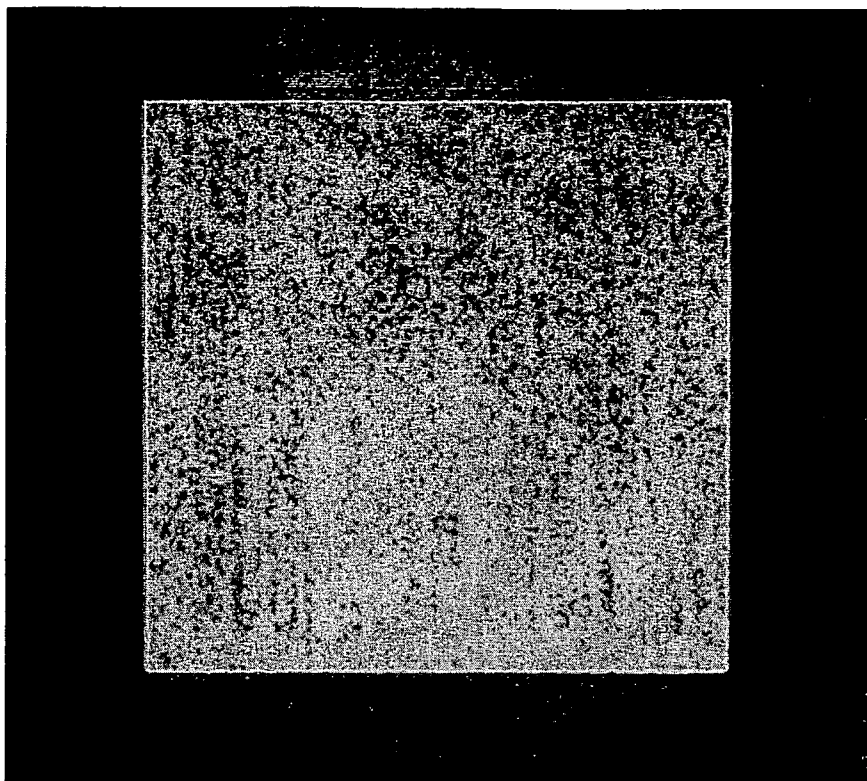


Figure 6: Anode current and anode voltage plot of a field emission device comprising arrays of CNT dots as disclosed in Example 4.

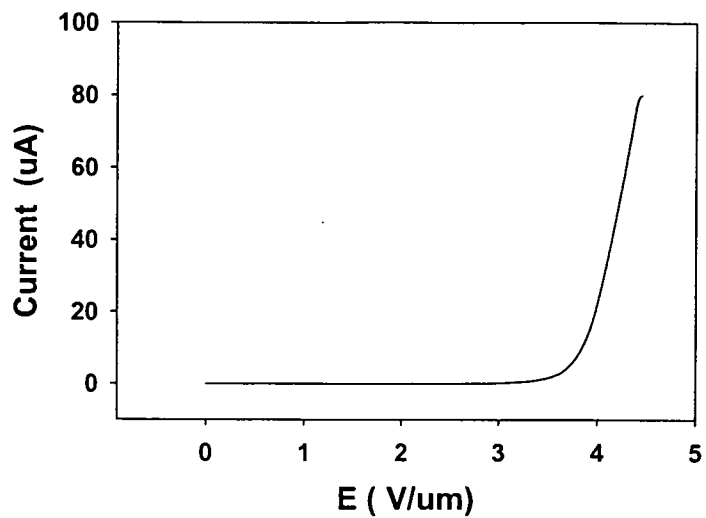


Figure 7: An image of the phosphor illumination by the field emission electrons from arrays of CNT dots as disclosed in Example 4.

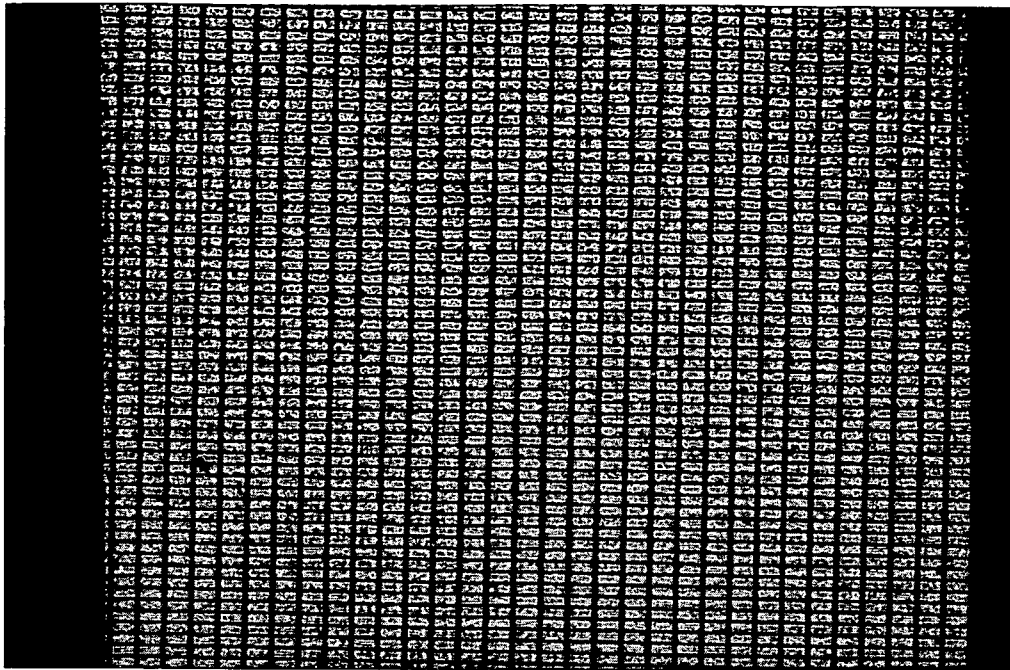


Figure 8: An image of the phosphor illumination by the field emission electrons from an array of CNT dots deposited on a top-gate triode substrate as disclosed in Example 5.

